STUDY OF THE EFFECT OF FLUX TYPE AND OXYGEN BLOWING ON SIMULTANEOUS REMOVAL OF PHOSPHORUS AND SULFORUS FROM MOLTEN IRON

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ABSTRACT

This research was conducted with the aim of studying the effect of lime based flux on with the composition of CaO*-20%*CaF_2*-8%*FeO *on the simultaneous removal process of phosphorus and sulfurous of hot metal. The effect of adding* Na_2O *to the composition of flux and oxygen blowing into melt on the results of the removal process was also studied. For these purposes the experiments were done using hot metal (product of the blast furnace of the isfahan steel company) in an induction furnace in the temperature range of 1350-1450°C. The results of these experiments show the possibility of the simultaneous removal of these impurities from hot metal using lime based flux. It was seen that adding* Na_2CO_3 *as supplaier of* Na_2O *into the flux composition causes a considerable improvement in the results of the process, because of the increase in the liquid phase volume in the slag, increase in the basic performance of the flux and the production of* CO_2 *gas. The blowing of oxygen into melt increases the removal of phosphorus to a small degree, but it is associated to the increase of melt temperature caused and the return of phosphorus from slag to hot metal. On the other hand increase in the melt oxygen potential, caused by the blowing of oxygen, decreases desulfurization to a considerable extent. The results show that in improved conditions there has been a 35% and 75% decrease in phosphorus and sulfurous respectively. The effect of the amount of primary silicon of melt on the results of the removal of phosphorus was studied further. Considering the analysis of the samples and using the empirical relations, it was clear that the hot metal silicon should be reduced to less than 15% to start phosphorus removal.*

INTRODUCTION

Pretreatment of molten iron before melt enters the convertor is one of the nessesitys of new steelmaking processes [1]. This process includes the decreasing of elements such as phosphorus and sulfurous which is done by away of increasing fluxes with a specific chemical composition [1, 2]. Today by using suitable thermodynamical conditions, the removal of phosphorus and sulfurous is done simultaneously and during one process. Na_2CO_3 is known to be a powerful reagent for the simultaneous removal of phosphorus and sulfurous [3, 4, 5], but environmental issues caused by the use of this composition and it's effect on the refractory walls have limited it's use. In recent years there has been a wide spread replacement of fluxes with a chemical composition based on lime and containing low amounts of CaF_2 [6, 7]. Therefore this research studies the effect of using basic flux based on lime with low oxide potential on the simultaneous removal of phosphorus and sulfurous. Furthermore the effect of using a low percent of Na_2O on flux and also the blowing of oxygen into heat on the results of the removal processes.

METHODOLOGY

Experiments of the simultaneous removal of phosphorus and sulfurous from molten iron (product of the blast furnace of the isfahan steel company) was done in an induction furnace with magnesite refractory and in the temperature range of 1350-1450°C and in three stages. In each stage of the experiments first samples were taken from the molten iron to identify it's exact chemical composition. Primary materials needed to produce flux containing lime were florin, oxide scale of iron and sodium carbonate that were used with a specific chemical composition and particle size distribution. Produced flux which was 10% of the melt weight (that is 2 kg), was divided into two equal amounts. The first part was added to the surface of the melt during 10 minuets and at the end of this time samples were taken from the hot metal and slag. After one stage of deslaging the rest of the flux was added to the melt in 10 minuets. At the end of this time final samples were taken from hot metal and slag. The slag composition of the stages of the research were as follows:

First stage: basic flux based on lime with low oxide potential with the composition of $CaO-20\%CaF_2-8\%FeO$.

Second stage: basic flux based on lime with low oxide potential containing a low percentage of Na_2CO_3 with the composition of $CaO-20\%CaF_2-8\%FeO-6\%Na_2O$.

Third stage: basic flux based on lime containing Na_2O accompanied by the blowing of oxygen in heat.

In the third stage for the purpose of oxygen blowing into melt and studying it's effect on the results of the removal processes, a steel lance with zirconia isolated covering was used. It should also be mentioned that in different parts of each stage of research two samples of hot metal and slag were taken to confirm the results. The average of the samples was used to identify the amount of element removal.

RESULTS AND DISCUSSION

First Stage

The results of the analysis of hot metal and slag samples in the first stage of this research has been shown in tables 1 and 2 respectively. The results show that there has been a 11% removal of phosphorus and a 35% removal of sulfurous (from samples A to C). There was also a 94% decrease in the amount of melt silicon. Figure 1 shows the effect of the time of experiment on the results of the removal of these elements.

Table 1: Chemical composition of hot metal samples in the first stage

Sample / Element	%P	%S	%Si	%C
A_1	0.300	0.049	0.350	3.890
A_2	0.302	0.048	0.350	3.910
A_{ave}	0.301	0.049	0.350	3.900
B_1	0.310	0.039	0.130	3.830
B_2	0.307	0.039	0.140	3.800
B_{ave}	0.309	0.039	0.135	3.815
C_1	0.277	0.031	0.020	3.680
C_2	0.275	0.032	0.030	3.630
C_{ave}	0.276	0.032	0.025	3.655

Table 2: Chemical composition of slag samples in the first stage

Sample / Element or component	%P	%S	%CaO	%SiO_2	%MgO	%FeO	%MnO
B_S	0.010	0.059	27.82	39.43	18.13	5.51	4.45
C_S	0.210	0.058	25.81	35.06	25.93	3.64	5.02

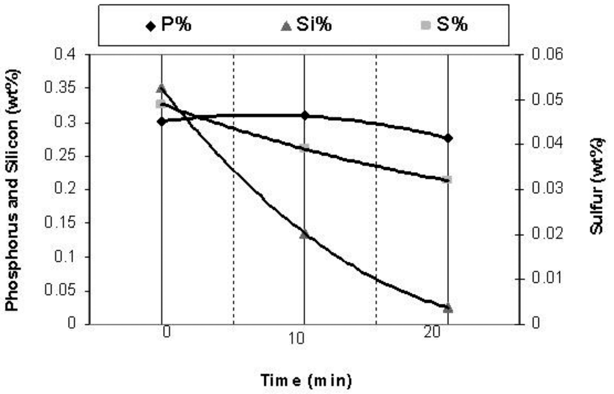

Figure 1: The phosphorus, sulfurous and silicon change against time in first stage

The phosphorus and sulfurous have been removed according to the following reactions [1, 2].

$$[P]+5/2[O]+3/2(O^{-2})=(PO_4^{-3}) \quad (1)$$

$$[S]+(O^{-2})=(S^{-2})+[O] \quad (2)$$

CaO present in the composition of flux is considered the supplying element of oxygen ion of slag. FeO used in flux is the supplying element of oxygen dissolved in melt. Studying the results of the first stage of this research was shows that first amount of preliminary silicon of heat should be reduced to a certain extent so that the removal of phosphorus can then be possible. This can be explained using the amount of Gibbs free energy change for the oxidation reaction of phosphorus and silicon.

$$Si_{(s)}+O_2=SiO_2 \qquad \Delta G^0_{(T=1350°C)} = -623.25\ KJ/mol \qquad (3)$$

$$1/2P_{2(g)}+5/2O_{2(g)}=PO_{5/2} \qquad \Delta G^0_{(T=1350°C)} = -360.56\ KJ/mol \qquad (4)$$

The phosphors and silicon activity in hot metal for raoultiant state was considered as follows [8].

$$a_{Si}=1.663\times10^{-5}\ ,\ a_P=1.24\times10^{-5}$$

Considering the phosphorus and silicon oxides are pure and the partial pressure of oxygen is one atmosphere the amount of ΔG of oxidation reaction of these elements is as bellow [8].

$$[Si]+O_{2(g)}=(SiO_2) \qquad \Delta G_{(T=1350°C)}= -476.740\ KJ/mol \qquad (5)$$

$$[P]+5/4O_{2(g)}=(PO_{5/2}) \qquad \Delta G_{(T=1350°C)}= -476.740\ KJ/mol \qquad (6)$$

It can be seen that in these conditions the silicon oxide is more stable than phosphorus oxide. Therefore to create the conditions necessary for the removal of phosphorus from hot metal it is necessary that first silicon be oxidized to a certain extent so after that both elements can be removed. This concluded because of the higher affinity of silicon to react with oxygen in the first 10 minuets of this experiment, phosphorus was not removed but the removal of sulfurous began from the start of the experiment and continued with a fairly fixed slope to the end.

Second Stage

In this stage of the research the effect of adding a small amount of Na_2O to the composition of flux based on lime was studied. The results of the analysis of samples of hot metal and slag in this stage is shown in Table 3 and 4 respectively. Figure 2 shows the change of phosphorus, sulfurous and silicon against time. In this stage we had a 35% removal of phosphorus and a 75% removal of sulfurous and the highest amount of decrease in melt silicon.

Table 3: Chemical composition of hot metal samples in the second stage

Sample / Element	%P	%S	%Si	%C
A_1	0.271	0.067	0.210	
A_2	0.270	0.067	0.140	3.690
A_{ave}	0.271	0.067	0.175	3.755
B_1	0.267	0.043	0.020	3.510
B_2	0.258	0.039	0.010	3.520
B_{ave}	0.263	0.041	0.015	3.515
C_1	0.185	0.018	0.002	3.240
C_2	0.166	0.015	0.002	3.260
C_{ave}	0.176	0.017	0.002	3.250

Table 4: Chemical composition of slag samples in the second stage

Element or component / Sample	%P	%S	%CaO	%SiO$_2$	%MgO	%FeO	%MnO
$B_{S\text{-}Na}$	0.090	0.079	39.07	22.90	8.50	7.16	4.59
$C_{S\text{-}Na}$	0.644	0.077	47.26	17.32	12.73	5.24	2.55

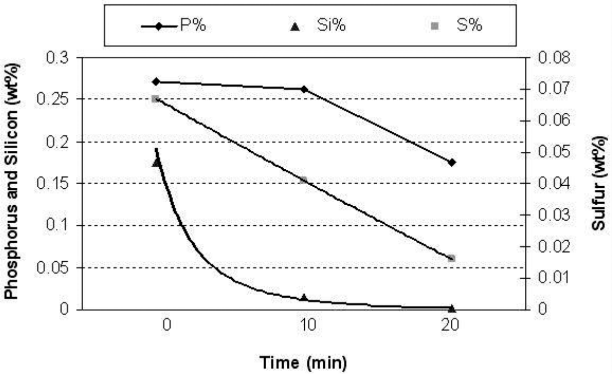

Figure 2: The phosphorus, sulfurous and silicon change against time in second stage

Na_2CO_3 is recognized as an effective element in the simultaneous removal of phosphorus and sulfurous. When using Na_2CO_3 it dissociates according to reaction 7 and causes the removal of phosphorus and sulfurous [5].

$$Na_2CO_3=Na_2O+CO_2 \quad (7)$$

$$3(Na_2O)+2[P]+5[O]=(3Na_2O.P_2O_5) \quad (8)$$

$$(Na_2O)+[S]+[C]=(Na_2S)+CO_{(g)} \quad (9)$$

On the other hand as Iwai and Kunisada [8] have emphasized in presence of Na_2O the removal of silicon increases according to the following reaction.

$$3(Na_2O)+2[S]+[Si]=2(Na_2S)+(Na_2O.SiO_2) \quad (10)$$

However about the effect of the presence of the Na_2O in the flux composition and the reasons of the improvement of the results of the removal process, these points are worth mentioning.

Increase in the melt phase volume of slag, increase in the melt phase volume in slag, caused by using Na_2O in the flux composition, is one of the causes of improvement in the results of the phosphorus and sulfurous removal process. Na_2CO_3 with 850°C melting point was in the molten phase in the temperature of the experiments, thus the melt phase volume in slag increased. On the other hand Na_2CO_3 decreases the melting point of the flux composition based on lime and on the whole mass transfer increase in the slag phase [5].

The Role of CO_2 Produced by the Dissociation of Na_2CO_3

Considering the fact that Na_2CO_3 has been used as the source of Na_2O, the role of CO_2 produced by the dissociation of Na_2CO_3 can be viewed in two ways. The first the production of CO_2 by the continuous adding of flux containing Na_2CO_3 has caused a kind of collision in the melt. This gas also acts as a mixer and improves the mass transfer which will have a useful effect on removal of both elements. The second the production of this gas causes melt oxygen potential to increase and improves the removal of phosphorus and silicon. Some researchees believe that adding Na_2O to the flux composition increases the basic power of slag and in this way has a suitable effect on the results of the removal processes.

Third Stage

The third stage of this research was conducted with flux similar to the second stage and accompanied by the blowing of oxygen into melt. The results of the analysis of melt and slag samples in this stage can be seen in Tables 5 and 6 respectively. As seen in Figure 3 the removal of phosphorus in this stage has increased a small amount and has reached 40% in comparison to the second stage. However desulfurization has decreased a considerable amount and has reached 45%. In studying, these points are worth mentioning.

The Maximum Solubility of Oxygen in Liquid Iron

Has been proven that in each temperature the maximum dissolution of oxygen in liquid iron is a fixed amount. Therefore it is wrong to expect that with blowing more oxygen in to melt the oxygen potential will rise and the removal of the phosphorus will improve. Temperature effects: the blowing of oxygen in this stage has caused increase in melt temperature this thermodynamically causes decrease in the removal of phosphorus.

Return of phosphorus to melt: the return of phosphorus to melt occurs because of increase in the activity of P_2O_5 in the slag. In the last seconds of the experiment the activity of lime and sodium carbonate of slag decreases and therefore the activity of P_2O_5 in slag increases and phosphorus returns to melt. At the same time because of increase in temperature, which is caused by the blowing of oxygen into compositions such as $CaO.P_2O_5$ composition lose their stability and thus phosphorus returns to melt. However the considerable decrease in desulfurization is caused by the increase in the oxygen potential of heat.

Table 5: Chemical composition of hot metal samples in the third stage

Sample / Element	%P	%S	%Si	%C
A_1	0.268	0.060	0.280	4.070
A_2	0.264	0.056	0.250	4.040
A_{ave}	0.266	0.058	0.265	4.055
B_1	0.215	0.051	0.040	3.850
B_2	0.200	0.050	0.050	3.720
B_{ave}	0.208	0.051	0.045	3.785
C_1	0.163	0.033	0.002	3.440
C_2	0.157	0.030	0.001	3.420
C_{ave}	0.160	0.032	0.002	3.430

Table 6: Chemical composition of slag samples in the third stage

Sample / Element or component	%P	%S	%CaO	%SiO2	%MgO	%FeO	%MnO
B_S	0.427	0.070	36.04	21.53	12.00	7.37	3.58
C_S	0.270	0.070	39.61	16.82	21.49	5.00	1.19

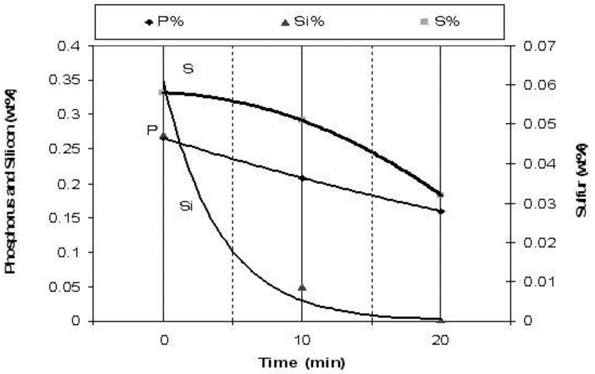

Figure 3: The phosphorus, sulfurous and silicon change against time in third stage

The amount of melt's silicon needed in the dephosphorization reaction by studying the results of stage one of this research it was found that from the beginning to the end of the first 10 minute of the experiment phosphorus was not removed and there was decrease in the amount of silicon up to 14%. Therefore in this part it was tried to prove that the phosphorus removal reaction had begun in slag B in stage one, by using the results of the analysis of slag samples in this stage and experimental reactions. To study the effect of the amount of melt's silicon, first the amount of the oxygen dissolved in melt was calculated. This was done using the equilibrium of reaction of carbon and CO and considering that melt was saturated of carbon. The amount of dissolved oxygen was 1.60×10^{-2}. Then using the experimental reactions of 11 and 12 [9] that calculate the amount of equilibrium constant of oxidation of phosphorus and activity coefficient of P_2O_5 in slag based on lime, the amount of equilibrium oxygen needed for the removal of phosphorus in this slag was calculated as 4.69×10^{-4}. The amount of oxygen dissolved in melt is sufficient to begin the removal reaction of phosphorus. Therefore lack of removal of phosphorus in stage one in slag B is associated to the amount of primary silicon of heat. Moreover, by using the silicon oxidation reaction and gaining the activity of SiO_2 from the ternary diagram [1] (Figure 4) and by substitution equilibrium oxygen of phosphorus under slag b in first stage to relation of silicon reaction, the amount of melt silicon content calculated as 0.14%. On the other hand, the amount of oxygen calculated from silicon reaction equilibrium and the amount of oxygen needed for the removal of phosphorus under slag B in the first stage are very close. Therefore it can be concluded that the result of this research shows that for beginning the phosphorus removal it is necessary that the amount of silicon in melt be reduced to lower than 0.15%.

$$\text{Log } K_{PO} = 7.93 \text{ Log } (\%CaO + 0.3\%MgO - 0.05\%FeO) + (21660/T) - 26.929 \tag{11}$$

$$\text{Log } \gamma P_{2O5} = -0.985\,(23X_{CaO} + 17X_{MgO} + 8X_{FeO}) - (22270/T) + 8.818 \tag{12}$$

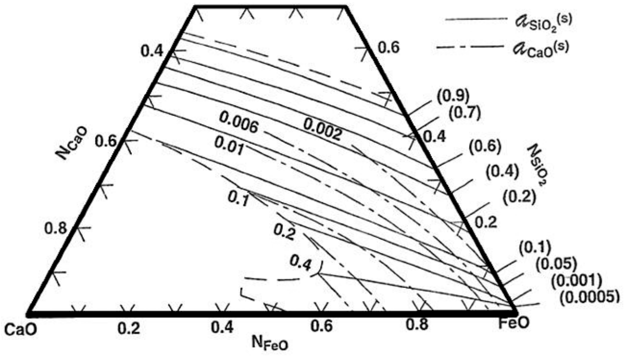

Figure 4: Activities of CaO and SiO_2 (by Gibbs-Duhem integration) in $CaO\text{-}FeO\text{-}SiO_2$ melts in equilibrium with liquid iron [1]

CONCLUSIONS

- Generally the simultaneous removal of phosphorus and sulfurous from molten iron with using basic flux based on lime is possible with a low oxide potential and without sodium carbonate.
- Adding a small amount of Na_2O to the flux composition based on lime increases the simultaneous removal of phosphorus and sulfurous considerably.
- The blowing of oxygen into melt increase the removal of phosphorus a small amount but decreases desulfurization considerably.
- By using basic flux based on lime containing 6 percent Na_2O the modified condition of the simultaneous removal of phosphorus and sulfurous was gained in this research and there was a 35% Removal of phosphorus and 75% removal of sulfurous.
- In was identified first the amount of primary silicon of heat should be decreased to less than 0.15% so that the removal of phosphorus can be possible.

NOMENCLATURE

$A_{(ave)}$ = The average analysis of hot metal samples before the beginning of process in the first stage.

$B_{(ave)}$ = The average analysis of hot metal samples in the middle of process in the first stage.

$C_{(ave)}$ = The average analysis of hot metal samples at the end of process in the first stage.

$A_{Na\,(ave)}$ = The average analysis of hot metal samples before the beginning of process in the second stage.

$B_{Na\,(ave)}$ = The average analysis of hot metal samples in the middle of process in the second stage.

$C_{Na\,(ave)}$ = The average analysis of hot metal samples at the end of process in the second stage

$A_{Na+O(ave)}$ = The average analysis of hot metal samples before the beginning of process in the third stage.

$B_{Na+O(ave)}$ = The average analysis of hot metal samples in the middle of process in the third stage.

$C_{Na+O(ave)}$ = The average analysis of hot metal samples at the end of process in the third stage.

B_S = The average analysis of slag samples in the middle of process in the first stage.

C = The average analysis of slag samples in the middle of process in the second stage.

C_{S-Na} = The average analysis of slag samples at the end of process in the second stage.

B_{S-Na+O} = The average analysis of slag samples in the middle of process in the third stage.

C_{S-Na+O} = The average analysis of slag samples at the end of process in the third stage.

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